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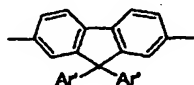
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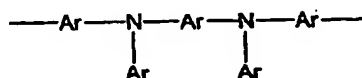
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(54) Title: POLYMERS THEIR PREPARATION AND USES



(I)



(II)

(57) Abstract: A polymer for use in an optical device comprising a first, optionally substituted, repeat unit of formula (I) and a second, optionally substituted, repeat unit of formula (II); wherein each Ar and Ar' is the same or different and comprises an optionally substituted aryl or heteroaryl group and optionally a third, optionally substituted, repeat unit in a molar ratio of no greater than 5 %, the third repeat unit having a formula -Ar-N(Ar)-Ar- and having a single nitrogen atom in its backbone.

Polymers, their preparation and uses

Field of the Invention

The invention relates to materials for optical devices, in particular organic electroluminescent devices, and the control of their physical and electronic properties.

Background of the Invention

One class of opto-electrical devices is those using an organic material for light emission or detection. The basic structure of these devices is a light emissive organic layer, for instance a film of a poly (p-phenylenevinylene) ("PPV") or polyfluorene, sandwiched between a cathode for injecting negative charge carriers (electrons) and an anode for injecting positive charge carriers (holes) into the organic layer. The electrons and holes combine in the organic layer generating photons. In WO 90/13148 the organic light-emissive material is a polymer. In US 4,539,507 the organic light-emissive material is of the class known as small molecule materials, such as (8-hydroxyquinoline) aluminium ("Alq3"). In a practical device one of the electrodes is transparent, to allow the photons to escape the device.

A typical organic light-emissive device ("OLED") is fabricated on a glass or plastic substrate coated with a transparent first electrode such as indium-tin-oxide ("ITO"). A layer of a thin film of at least one electroluminescent organic material covers the first electrode. Finally, a cathode covers the layer of electroluminescent organic material. The cathode is typically a metal or alloy and may comprise a single layer, such as aluminium, or a plurality of layers such as calcium and aluminium. Other layers can be added to the device, for example to improve charge injection from the electrodes to the electroluminescent material. For example, a hole injection layer such as poly(ethylene dioxythiophene) / polystyrene sulfonate (PEDOT-PSS) or polyaniline may be provided between the anode and the electroluminescent material. When a voltage is applied between the electrodes from a power supply one of the electrodes acts as a cathode and the other as an anode.

For organic semiconductors important characteristics are the binding energies, measured with respect to the vacuum level of the electronic energy levels, particularly the "highest occupied molecular orbital" (HOMO) and the "lowest unoccupied molecular

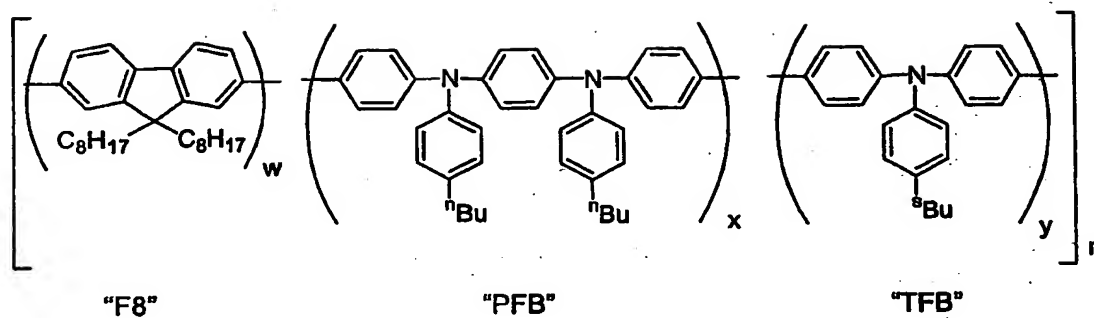
orbital" (LUMO) level. These can be estimated from measurements of photoemission and particularly measurements of the electrochemical potentials for oxidation and reduction. It is well understood in this field that such energies are affected by a number of factors, such as the local environment near an interface, and the point on the curve (peak) from which the value is determined. Accordingly, the use of such values is indicative rather than quantitative.

In operation, holes are injected into the device through the anode and electrons are injected into the device through the cathode. The holes and electrons combine in the organic electroluminescent layer to form an exciton which then undergoes radiative decay to give light. One way of improving efficiency of devices is to provide hole and electron transporting materials – for example, WO 99/48610 discloses blending of hole transporting polymers, electron transporting polymers and electroluminescent polymers. A 1:1 copolymer of dioctylfluorene and triphenylamine is used as the hole transporting polymer in this document.

A focus in the field of polymer OLEDs is the development of full colour displays for which red, green and blue emissive materials are required. One drawback with existing polymer OLED displays relevant to this development is the relatively short lifetime of blue emissive materials known to date (by "lifetime" is meant the time for the brightness of the OLED to halve at constant current when operated under DC drive).

In one approach, the lifetime of the emissive material may be extended by optimisation of the OLED architecture; for example lifetime of the blue material may in part be dependant on the cathode being used. However, the advantage of selecting a cathode that improves blue lifetime may be offset by disadvantageous effects of the cathode on performance of red and green materials. For example, Synthetic Metals 111-112 (2000), 125-128 discloses a full colour display wherein the cathode is LiF / Ca / Al. The present inventors have found that this cathode is particularly efficacious with respect to the blue emissive material but which shows poor performance with respect to green and, especially, red emitters.

Another approach is development of novel blue electroluminescent materials. For example, WO 00/55927, which is a development of WO 99/48160, discloses a blue electroluminescent polymer of formula (a):



(a)

wherein $w + x + y = 1$, $w \geq 0.5$, $0 \leq x + y \leq 0.5$ and $n \geq 2$

In essence, the separate polymers disclosed in WO 99/48160 are combined into a single molecule. The F8 repeat unit is provided for the purpose of electron injection; the TFB unit is provided for the purpose of hole transport; and the PFB repeat unit is provided as the emissive unit.

WO 99/54385 and EP 1229063 disclose copolymers of fluorenes and amines.

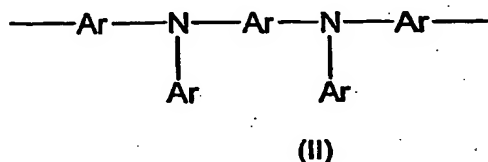
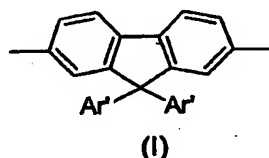
It is an object of the present invention to provide a means for increasing the lifetime of polymers for use in an optical device above that of prior art polymers. It is a further object of the invention to provide a long-lived polymer for use in an optical device, particularly a long-lived blue electroluminescent material. It is a yet further object of the invention to provide a means for increasing the thermal stability of prior art polymers.

Summary of the Invention

The present inventors have surprisingly found that the lifetime of a polymer for use in an optical device, in particular an electroluminescent polymer, may be increased by the incorporation of repeat units that increase the glass temperature (T_g) of the polymer. In particular, incorporation of 2,7-linked 9,9-diarylfluorene repeat units into an electroluminescent polymer, particularly a blue emissive electroluminescent polymer, results in significant increase in that polymer's lifetime. Furthermore, the present inventors have found that it is unnecessary to have separate hole transporting units and blue emissive units; it has been found that both functions may be performed by the PFB

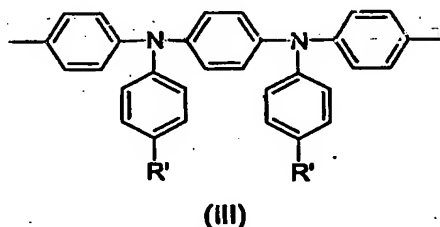
unit. Surprisingly, the omission of TFB from the prior art polymers described above is found to result in a significant improvement in lifetime.

Accordingly, in a first aspect the invention provides a polymer for use in an optical device comprising a first, optionally substituted, repeat unit of formula (I) and a second, optionally substituted, repeat unit of formula (II):



wherein each Ar and Ar' is the same or different and comprises an optionally substituted aryl or heteroaryl group and, optionally, a third, optionally substituted, repeat unit in a molar ratio of no greater than 5 %, the third repeat unit having a formula $-\text{Ar}-\text{N}(\text{Ar})-\text{Ar}-$ and having a single nitrogen atom in its backbone.

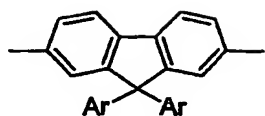
Preferably, each Ar is phenyl. More preferably, the second repeat unit comprises a repeat unit of formula (III):



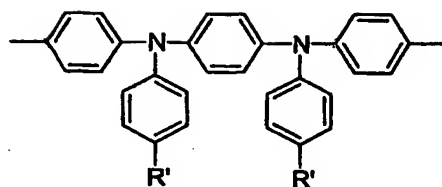
wherein each R' is independently selected from hydrogen or a solubilising group.

Preferably, the third repeat unit is absent. Preferably, the polymer comprises no repeat units comprising nitrogen atoms in the repeat unit backbone other than the repeat unit of formula (II).

Accordingly, in a first aspect the invention provides a polymer for use in an optical device comprising an optionally substituted repeat unit of formula (I) and an optionally substituted repeat unit of formula (II):



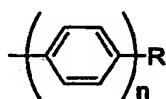
(I)



(II)

wherein each Ar and Ar' is the same or different and comprises an optionally substituted aryl or heteroaryl group and optionally a third, optionally substituted, repeat unit in a molar ratio of no greater than 5 %, the third repeat having formula $-\text{Ar}-\text{N}(\text{Ar})-\text{Ar}-$ and having a single nitrogen atom in its backbone.

Preferably, each Ar is independently selected from the group comprising an optionally substituted residue of formula (IV):



(IV)

wherein $n = 1, 2$ or 3 and R is a solubilising group or hydrogen. Preferred solubilising groups R are selected from optionally substituted alkyl or alkoxy, preferably butyl.

Preferably, each R' is optionally substituted alkyl or alkoxy, more preferably butyl, most preferably n-butyl.

Preferably, the polymer according to the first aspect of the invention comprises less than 50 mol %, more preferably 10-40 mol %, of repeat units of formula (I).

The present inventors have surprisingly found that reducing the amine content within a polymer results in an increase in the efficiency of that material in certain device architectures, in particular devices with cathodes having a relatively high workfunction resulting in relatively poor electron injecting ability such as barium ($wf = 2.7$ eV), strontium ($wf = 2.59$ eV) or calcium ($wf = 2.87$ eV) (source: J. Appl. Phys. 48(11) 1997, 4730.) Accordingly, in one preferred embodiment the polymer according to the first aspect of the invention comprises less than 30 mol %, more preferably less than 10 mol %, of repeat units of formula (II).

Preferably, the polymer according to the first aspect of the invention comprises a further repeat unit selected from optionally substituted 9,9-dialkyl- or 9,9-dialkoxy-2,7-fluorenyl, more preferably 9,9-di(n-octyl)fluorene.

Preferably, the polymer according to the first aspect of the invention is an electroluminescent polymer, more preferably a polymer capable of emitting light in the wavelength range 400-500 nm, most preferably 430-500 nm

In a second aspect, the invention provides an electroluminescent device comprising a first electrode for injection of positive charge carriers, a second electrode for injection of negative charge carriers and an electroluminescent region located between the first and second electrode comprising a polymer according to the first aspect of the invention. Preferably, the polymer according to the first aspect of the invention is the only semiconducting polymer in the electroluminescent region.

By "electroluminescent region" is meant that layer of an electroluminescent device comprising a polymer comprising a repeat unit of formula (II) from which electroluminescence is obtained. For the avoidance of doubt, it will be appreciated that, where present, a hole injection material (such as PEDOT-PSS or polyaniline), a hole transporting layer or an electron transporting layer separate from the electroluminescent layer do not constitute a part of the electroluminescent region.

Brief Description of the Drawings

The present invention will now be described in further detail, by way of example only, with reference to the accompanying drawings in which:

FIGURE 1 shows a prior art electroluminescent device

FIGURE 2 shows a plot of luminance vs. time for a blue electroluminescent device according to the invention

Detailed Description of the Invention

Polymers according to the invention are preferably copolymers comprising an arylene co-repeat unit Ar such as a fluorene, particularly 2,7-linked 9,9 dialkyl fluorene or 2,7-linked 9,9 diaryl fluorene; a spirofluorene such as 2,7-linked 9,9-spirofluorene; an

Indenofluorene such as a 2,7-linked indenofluorene; or a phenyl such as alkyl or alkoxy substituted 1,4-phenylene. Each of these groups may be substituted.

Further suitable Ar groups are known in this art, for example as disclosed in WO 00/55927 and WO 00/46321, the contents of which are incorporated herein by reference.

A polymer according to the present invention may comprise a homopolymer, copolymer, terpolymer or higher order polymer.

A copolymer, terpolymer or higher order polymer according to the present invention includes regular alternating, random and block polymers where the percentage of each monomer used to prepare the polymer may vary.

For ease of processing, it is preferred that the polymer is soluble. Substituents such as C₁₋₁₀ alkyl or C₁₋₁₀ alkoxy may usefully be selected to confer on the polymer solubility in a particular solvent system. Typical solvents include mono- or poly-alkylated benzenes such as toluene and xylene or THF.

Two polymerisation techniques that are particularly amenable to preparation of conjugated polymers from aromatic monomers are Suzuki polymerisation as disclosed in, for example, WO 00/53656 and Yamamoto polymerisation as disclosed in, for example, "Macromolecules", 31, 1099-1103 (1998). Suzuki polymerisation entails the coupling of halide and boron derivative functional groups; Yamamoto polymerisation entails the coupling of halide functional groups. Accordingly, it is preferred that each monomer is provided with two reactive functional groups P wherein each P is independently selected from the group consisting of (a) boron derivative functional groups selected from boronic acid groups, boronic ester groups and borane groups and (b) halide functional groups.

With reference to Figure 1, the standard architecture of an optical device according to the invention, in particular an electroluminescent device, comprises a transparent glass or plastic substrate 1, an anode of indium tin oxide 2 and a cathode 4. The polymer according to the invention is located in layer 3 between anode 2 and cathode 4. Layer 4 may comprise the polymer according to the invention alone or a plurality of polymers. Where a plurality of polymers are deposited, they may comprise a blend of at least two of a hole transporting polymer, an electron transporting polymer and, where the device is

a PLED, an emissive polymer as disclosed in WO 99/48160. Alternatively, layer 3 may be formed from a single polymer that comprises regions selected from two or more of hole transporting regions, electron transporting regions and emissive regions as disclosed in, for example, WO 00/55927 and US 6353083. Each of the functions of hole transport, electron transport and emission may be provided by separate polymers or separate regions of a single polymer. Alternatively, more than one function may be performed by a single region or polymer. In particular, a single polymer or region may be capable of both charge transport and emission. Each region may comprise a single repeat unit, e.g. a triarylamine repeat unit may be a hole transporting region. Alternatively, each region may be a chain of repeat units, such as a chain of polyfluorene units as an electron transporting region. The different regions within such a polymer may be provided along the polymer backbone, as per US 6353083, or as groups pendant from the polymer backbone as per WO 01/62869.

In addition to layer 3, a separate hole transporting layer and / or an electron transporting layer may be provided.

Although not essential, a layer of organic hole injection material (not shown) between the anode 2 and the polymer layer 3 is desirable because it assists hole injection from the anode into the layer or layers of semiconducting polymer. Examples of organic hole injection materials include poly(ethylene dioxythiophene) (PEDT / PSS) as disclosed in EP 0901176 and EP 0947123, or polyaniline as disclosed in US 5723873 and US 5798170.

Cathode 4 is selected from materials that have a workfunction allowing injection of electrons into the electroluminescent layer. Other factors influence the selection of the cathode such as the possibility of adverse interactions between the cathode and the electroluminescent material. The cathode may consist of a single material such as a layer of aluminium. Alternatively, it may comprise a plurality of metals, for example a bilayer of calcium and aluminium as disclosed in WO 98/10621, elemental barium disclosed in WO 98/57381, Appl. Phys. Lett. 2002, 81(4), 634 and WO 02/84759 or a thin layer of dielectric material to assist electron injection, for example lithium fluoride disclosed in WO 00/48258 or barium fluoride, disclosed in Appl. Phys. Lett. 2001, 79(5), 2001.

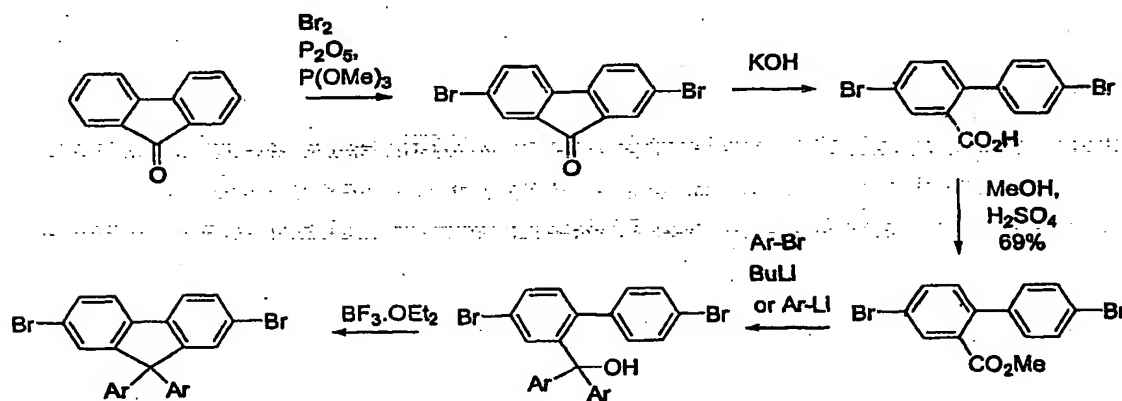
A typical electroluminescent device comprises an anode having a workfunction of 4.8 eV. Accordingly, the HOMO level of the hole transporting region is preferably around 4.8-5.5 eV. Similarly, the cathode of a typical device will have a workfunction of around 3 eV. Accordingly, the LUMO level of the electron transporting region is preferably around 3-3.5 eV.

Electroluminescent devices may be monochrome devices or full colour devices (i.e. formed from red, green and blue electroluminescent materials).

Examples

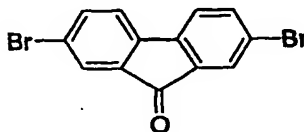
Monomer Examples

Monomers according to the invention were prepared in accordance with the scheme below:



Monomer Example M1: 2,7-dibromo-9,9-diphenylfluorene

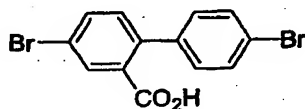
2,7-Dibromofluorenone



In a 3L flange flask fluorenone (100.006g, 0.555 mol), phosphorus pentoxide (110.148g, 0.776 mol) and trimethylphosphate (1200 mL) were mixed. Under mechanical stirring, a solution of bromine (63 mL, 1.23 mol) in trimethylphosphate (200 mL) was quickly added. This clear solution was then heated for 22 hours at 120 °C. The mixture was allowed to cool to room temperature, then poured into 3L of water. When sodium thiosulfate was added (50.045g) the mixture turned yellow. Stirring was maintained for 1 hour then the yellow solid was filtered. This solid was heated in methanol to remove the mono-brominated compound and gave 176.183g (98% pure by HPLC, 94% yield).

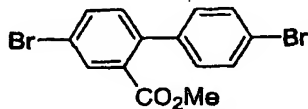
¹H NMR (CDCl₃) 7.73 (2H, d, J 2.0), 7.61 (2H, dd, J 7.6, 2.0), 7.36 (2H, d, J 8.0); ¹³C NMR (CDCl₃) 142.3, 137.5, 135.3, 127.9, 123.3, 121.8, 109.8.

4,4'-Dibromo-2-carboxylic acid-1, 1'-biphenyl



In a 2L flange flask 2,7-dibromofluorenone (120.526g, 0.356 mol), potassium hydroxide (finely powdered flakes, 168.327g, 3.000 mol) and toluene (600 mL) were placed. This mixture was heated at 120 °C for four hours then left to cool to room temperature. Water was added to dissolve the solid (~ 2L) under vigorous stirring. The greenish aqueous layer was removed and the yellow toluene layer was washed twice with water. The combined aqueous layers were acidified with concentrated hydrochloric acid then the precipitated solid was filtered, dried then recrystallised from toluene to give 100.547g of off white crystals (79% yield); ¹H NMR ((CD₃)₂CO) 8.00 (1H, d, J 2.0), 7.77 (1H, dd, J 8.0, 2.4), 7.57 (2H, d, J 8.0), 7.34 (1H, d, J 8.4), 7.29 (2H, d, J 8.8) ; ¹³C NMR ((CD₃)₂CO) 167.1, 140.4, 139.8, 134.2, 133.5, 132.8, 132.7, 131.2, 130.6, 121.4, 121.1.

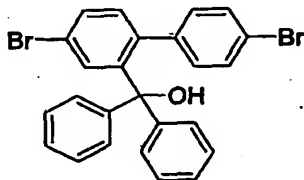
Methyl ester of 4,4'-dibromo-2-carboxylic acid -1,1'-biphenyl



4,4'-dibromo-2-carboxylic acid biphenyl (171.14g, 0.481 mol) was suspended in methanol (700 mL) and sulfuric acid (15 mL) then heated at 80 °C for 21 hours. The

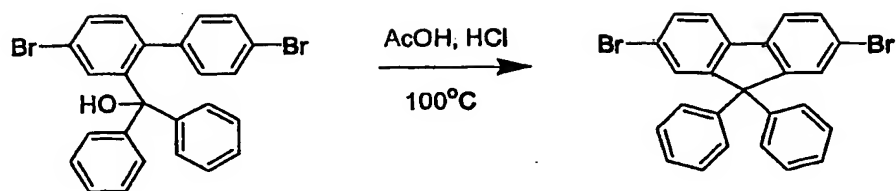
solvent was removed and the oil was dissolved in ethyl acetate. This solution was washed with 2N sodium hydroxide, water, saturated sodium chloride, dried over magnesium sulfate, filtered and evaporated to give an orange oil. This oil was treated with hot methanol, on cooling the ester precipitated out and was filtered. The mother liquor was evaporated and the solid recrystallised giving additional product. The ester was 100% pure by GCMS, a yield of 123.27g (69%) was obtained; ^1H NMR (CDCl_3) 7.99 (1H, d, J 2.0), 7.64 (1H, dd, J 8.0, 1.6), 7.51 (2H, d, J 8.4), 7.19 (1H, d, J 8.8), 7.13 (2H, d, J 8.8), 3.67 (3H, s); ^{13}C NMR (CDCl_3) 167.1, 140.3, 139.1, 134.4, 132.9, 132.1, 132.0, 131.3, 129.8, 121.9, 121.5, 52.3; GCMS: $M^+ = 370$

4,4'-dibromo-2-diphenyl alcohol -1,1'-biphenyl



4,4'-dibromo-2-methyl ester-biphenyl (24.114g, 65.1 mmol) was dissolved in dry diethyl ether (120 mL) and the solution was cooled to -60°C by using an isopropanol/dry ice bath. Phenyl lithium (1.8M solution in cyclohexane-ether, 91 mL) was then added dropwise. The mixture was stirred and let to warm to room temperature. The reaction was complete after four hours. Water was added (70 mL) then the aqueous layer washed once with diethyl ether. Combined organic phases were washed with sodium chloride, dried over magnesium sulfate, filtered and evaporated to give a yellow powder. Recrystallisation from isopropanol afforded 19g of white solid (59% yield); GC-MS (m/z , relative intensity %) 494 (M^+ , 100); ^1H NMR (CDCl_3) 7.43 (1H, dd, J 8.4, 2.4), 7.28 (6H, m), 7.23 (2H, d, J 8.0), 7.11 (4H, m), 6.99 (1H, d, J 2.4), 6.94 (1H, d, J 8.4), 6.61 (2H, d, J 8.4); ^{13}C NMR (CDCl_3) 147.5, 146.7, 140.3, 139.3, 134.0, 133.0, 131.2, 131.1, 130.3, 128.2, 128.1, 127.8, 121.8, 121.3, 83.2.

2,7-dibromo-9,9-diphenylfluorene



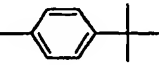
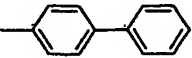
The alcohol (69.169g, 140mmol) and glacial acetic acid (450ml) were stirred and heated to reflux, then concentrated hydrochloric acid (0.5ml) was added dropwise. When the addition was completed the mixture was heated for one hour and then cooled. The reaction mixture was poured into water (500ml), after which the solid was filtered off. The white solid was recrystallised from *n*-butyl acetate three times to give 20.03g of desired product (99.59% by HPLC, 30% yield).

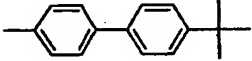
^1H NMR (CDCl_3), δ/ppm : 7.58 (2H, d, J 7.6), 7.49 (2H, d, 1.2), 7.48 (2H, dd, 1.6), 7.25 (6H, m), 7.14 (4H, m).

^{13}C NMR (CDCl_3), δ/ppm : 153.2, 144.6, 138.3, 131.1, 129.6, 128.7, 128.2, 127.4, 122.0, 121.7, 65.8.

Monomer Examples M2-M4

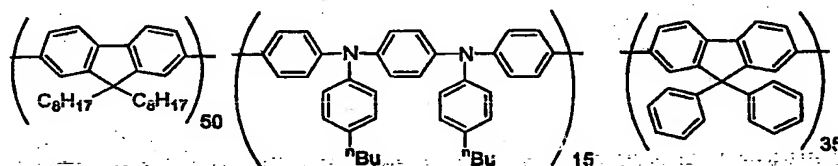
Monomers with Ar groups as detailed in the table below were prepared in accordance with the scheme and general experimental process outlined above. Aryllithium compounds corresponding to Ar groups shown in the table were prepared from the corresponding aryl bromide.

Monomer example no.	Ar	Yield of monomer
M2		90%
M3		24%

M4		22%
----	---	-----

Polymer Example P1

A blue electroluminescent polymer according to the invention was prepared in accordance with the process of WO 00/53656 by reaction of 9,9-di-n-octylfluorene-2,7-di(ethylenylboronate) (0.5 equivalents), 2,7-dibromo-9,9-diphenylfluorene (0.35 equivalents) and N,N'-di(4-bromophenyl)-N,N'-di(4-n-butylphenyl)-1,4-diaminobenzene (0.15 equivalents) to give polymer P1:



P1

Device Example

Onto indium tin oxide supported on a glass substrate (available from Applied Films, Colorado, USA) was deposited a layer of PEDT / PSS, available from Bayer ® as Baytron P ® by spin coating. A layer of polymer P1 was deposited over the PEDT / PSS layer by spin-coating from xylene solution. Onto the polymer P1 was deposited a cathode consisting of a first layer of lithium fluoride, a second layer of calcium and a third, capping layer of aluminium.

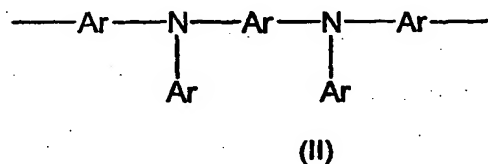
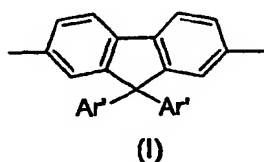
For the purpose of comparison with P1, an identical device was prepared except that the electroluminescent polymer comprised 10 % TFB repeat units (full composition: 10 % TFB; 50 % F8; 30 % PFB; 10 % PFB – disclosed in WO 02/92723).

As can be seen from Figure 1, removal of TFB from the polymer results in a significant improvement in lifetime.

Although the present invention has been described in terms of specific exemplary embodiments, it will be appreciated that various modifications, alterations and / or combinations of features disclosed herein will be apparent to those skilled in the art without departing from the spirit and scope of the invention as set forth in the following claims.

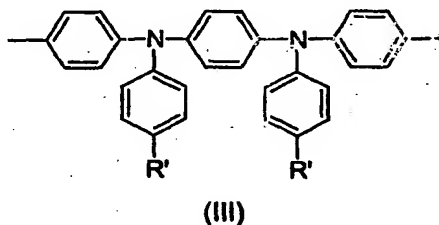
Claims

- 1) A polymer for use in an optical device comprising a first, optionally substituted, repeat unit of formula (I) and a second, optionally substituted, repeat unit of formula (II):



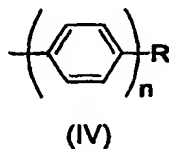
wherein each Ar and Ar' is the same or different and comprises an optionally substituted aryl or heteroaryl group and optionally a third, optionally substituted, repeat unit in a molar ratio of no greater than 5 %, the third repeat unit having a formula $-Ar-N(Ar)-Ar-$ and having a single nitrogen atom in its backbone.

- 2) A polymer according to claim 1 wherein the second repeat unit comprises a repeat unit of formula (III):



wherein each R' is independently selected from hydrogen or a solubilising group.

- 3) A polymer according to claim 1 or 2 wherein the third repeat unit is absent.
- 4) A polymer according to claim 1 wherein each Ar' is independently selected from the group comprising an optionally substituted residue of formula (IV):



wherein $n = 1, 2$ or 3 and R is a solubilising group or hydrogen

- 5) A polymer according to claim 4 wherein R is selected from the group consisting of optionally substituted alkyl or alkoxy.
- 6) A polymer according to claim 4 wherein R is hydrogen or butyl.
- 7) A polymer according to any preceding claim wherein each R' is optionally substituted alkyl or alkoxy.
- 8) A polymer according to claim 7 wherein R' is n-butyl.
- 9) A polymer according to any preceding claim comprising less than 50 mol % of repeat units of formula (I).
- 10) A polymer according to any preceding claim comprising less than 30 mol % of repeat units of formula (II).
- 11) A polymer according to any preceding claim comprising less than 10 mol % of repeat units of formula (II).
- 12) A polymer according to any preceding claim comprising a further repeat unit selected from optionally substituted 9,9-dialkyl- or 9,9-dialkoxy-2,7-fluorenyl.
- 13) A polymer according to claim 12 wherein the further repeat unit is 9,9-di(n-octyl)fluorene.
- 14) A polymer according to claim 9 comprising 10-40 mol % of repeat units of formula (I).
- 15) A polymer according to any preceding claim capable of emitting light in the wavelength range 400-500 nm, preferably 430-500 nm.
- 16) An optical device comprising a first electrode for injection of positive charge carriers, a second electrode for injection of negative charge carriers and a layer located between the first and second electrode comprising a polymer as defined in any one of claims 1-15.
- 17) An optical device according to claim 16 that is an electroluminescent device.
- 18) An optical device according to claim 17 wherein the polymer according to any one of claims 1-15 is the only semiconducting polymer in the electroluminescent region.

Fig. 1

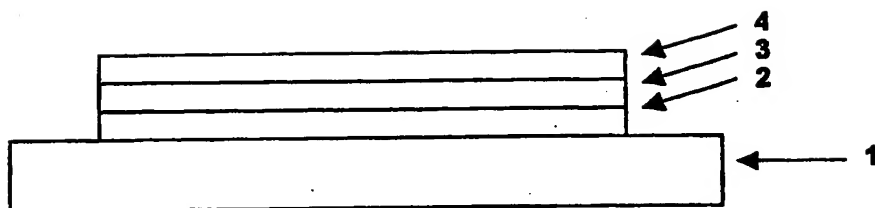
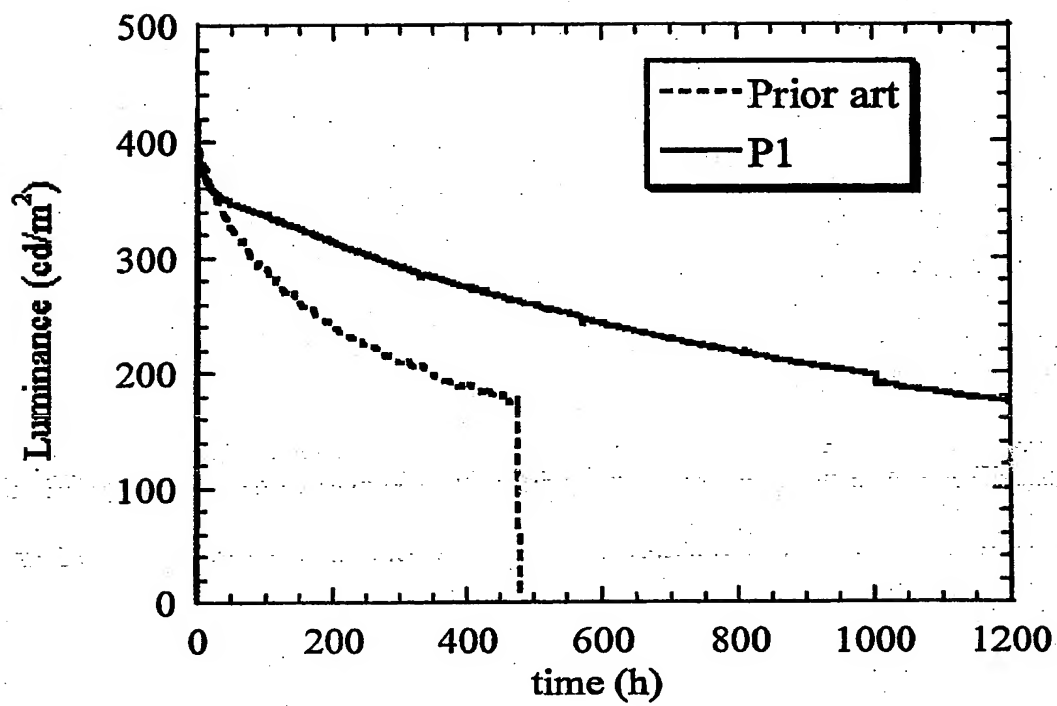


Fig. 2



A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09K11/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☐ Further documents are listed in the continuation of box C.

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Date of the actual completion of the International search

17 July 2003

Date of mailing of the International search report

24/07/2003

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INTERNATIONAL SEARCH REPORT

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